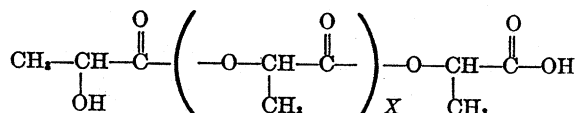# Lactic Acid as a Component of Synthetic Resins
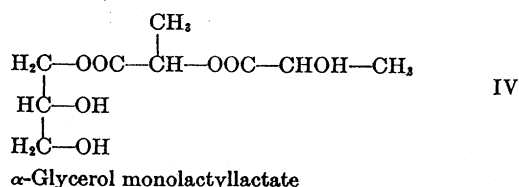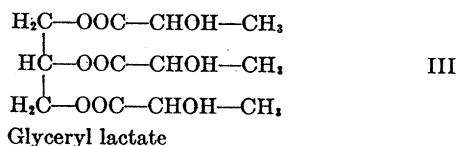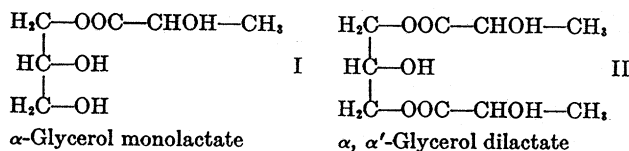
J. T. STEARN, B. MAKOWER, AND P. H. GROGGINS

THE use of lactic acid—i. e., α-hydroxypropionic acid, CH₃.CHOH.COOH—as a component of synthetic resins has already been mentioned in the chemical and patent literature. Lactic acid is known to be used in the manufacture of cast phenoplastic resins. In this and other reported applications advantage has apparently been taken only of the carboxyl group, the lactic acid functioning as an acid catalyst (*18*) or as a modifying agent to replace other monocarboxylic acids, such as the lower fatty acids, chlorinated fatty acids, and benzoic acid (*2, 3*). The utilization of the bifunctional character of lactic acid—that is, of its hydroxyl as well as of its carboxyl group—has been limited to the preparation of lactyllactic acid, lactide balsams, and dilactide by intermolecular esterification. These reactions were recently reviewed by Hovey and Hodgins (*10*). Dorough (*5*) prepared a resin of high molecular weight (about 4000) from lactic acid alone, and it is presumed that such successive interesterifications yield long-chain molecules of the following type:

$$CH_3-CH-\overset{O}{\underset{OH}{C}}-\left(-O-CH-\overset{O}{\underset{CH_3}{C}}-\right)_X -O-CH-\overset{O}{\underset{CH_3}{C}}-OH$$

The utilization of the bifunctionality of high-molecular-weight hydroxycarboxylic acids such as natural rosin acids (Congo copal) for the preparation of synthetic resins was suggested by Krumbhaar (*15*).

$$H_2C-OOC-CHOH-CH_3$$
$$HC-OH \qquad I$$
$$H_2C-OH$$
α-Glycerol monolactate

$$H_2C-OOC-CHOH-CH_3$$
$$HC-OH \qquad II$$
$$H_2C-OOC-CHOH-CH_3$$
α, α'-Glycerol dilactate

$$H_2C-OOC-CHOH-CH_3$$
$$HC-OOC-CHOH-CH_3 \qquad III$$
$$H_2C-OOC-CHOH-CH_3$$
Glyceryl lactate

$$CH_3$$
$$H_2C-OOC-CH-OOC-CHOH-CH_3$$
$$HC-OH \qquad IV$$
$$H_2C-OH$$
α-Glycerol monolactyllactate

The use of lactic acid as a component of alkyd resins has been investigated. In synthesizing these resins advantage is taken of the hydroxyl as well as of the carboxyl function of this acid. The present study indicates that these three-component resins compare favorably with the similar two-component alkyds and that the extent to which lactic acid may be used will be governed by its price. An economic study of the conversion of lactic acid to methyl acrylate indicates that, based on raw material costs, this process cannot compete favorably with the syntheses from either ethylene or ethylene oxide.

Alkyd Resins

Glycerol can form a series of esters with lactic acid, all of which have the same number of hydroxyl groups as the parent alcohol. The product of these reactions may be mono-, di-, or trilactates or lactyllactates of glycerol or mixtures of these, depending on the proportions used and other factors. Figure 1 shows examples of possible esters.

Any one of these esters is capable of combining further with polycarboxylic acids in the same manner as glycerol to form alkyd resins.

Of the numerous possibilities, the chosen starting material for the preparation of alkyd resins was the esterification product of one mole of glycerol with two moles of lactic acid. As will be shown later, the most probable formula for this product is α,α'-glycerol dilactate, Figure 1, formula II.

When glycerol dilactate is esterified with dicarboxylic acids, alkyd resins are obtained. Inasmuch as these resins are synthesized from three components—namely, polyhydric alcohol, hydroxycarboxylic acid, and dicarboxylic acid—they will be called "three-component alkyds" in this paper. The alkyd resins derived from only two types of molecules—namely, polyhydric alcohol and dicarboxylic acid—will be called "two-component alkyds", regardless of the fact that in their commercially used forms they contain further additions.

Kienle and co-workers (*12*) assumed that in the esterification reaction of glycerol with dicarboxylic acids, there exists an intermediate compound, consisting of a combination of two molecules of glycerol with three molecules of dicarboxylic acid. In this intermediate compound the secondary β-hydroxyls of glycerol have remained unreacted. It is a

straight-chain dihydroxydicarboxylic acid corresponding to the following formula:

$$HOOC \quad COO.CH_2.CH.CH_2.OOC \quad COO.CH_2.CH.CH_2.OOC \quad COOH$$

(with OH groups shown)
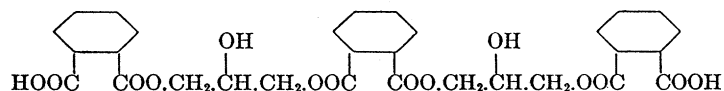
Gelation does not occur until the remaining carboxyl groups begin to react with the β-hydroxyl groups of this intermediate compound. The authors, therefore, call it the monomer of this polymerization reaction. In glycerol dilactate, however, the primary hydroxyl groups of glycerol have been replaced by secondary hydroxyl groups, and consequently the existence of such a "monomer" cannot be assumed here. If the hydroxyl groups are all secondary, as in formula II, they may be expected to react with approximately equal rapidity. It is probable, therefore, that the esterification of glycerol dilactate with dicarboxylic acid occurs in a random fashion and gives rise to branched-chain molecules. If such a condition prevails, insolubility and infusibility of the resin polymer may be expected to take place at a lower average molecular weight than in the case of the three-component resins. In addition, there is the possibility of ester exchange between glycerol dilactate and the dicarboxylic acid which tends to increase further the number and variety of reaction products.

Two of the simplest structural formulas of the derived condensation products which are possible are shown in Figure 2. Such three-component alkyds, in which lactic acid or another hydroxycarboxylic acid is a component, have been covered by a patent (9).

Glyceryl lactylphthalate, molecular weight 899

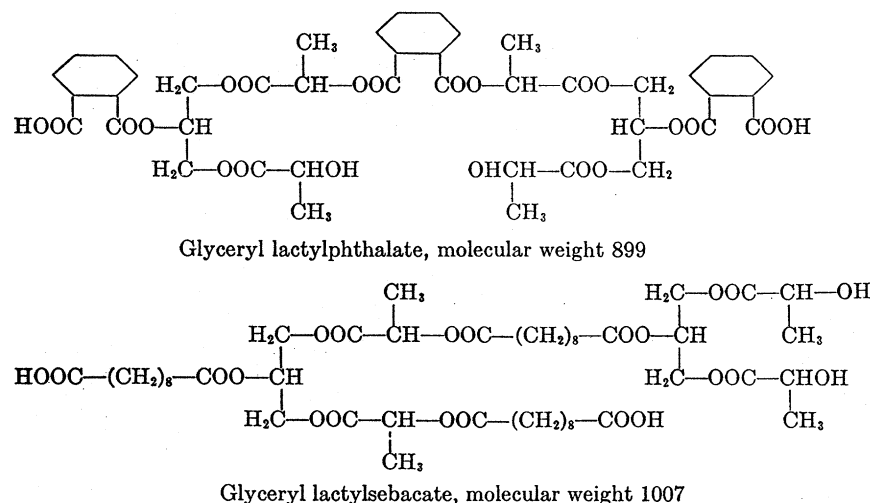Glyceryl lactylsebacate, molecular weight 1007

FIGURE 2. POSSIBLE STRUCTURAL FORMULAS OF THREE-COMPONENT RESINS

OUTLINE OF WORK. It has already been shown that the reaction between glycerol and lactic acid may lead to a number of glycerol lactates, all of which have the same number of hydroxyl groups as were present originally in the polyhydric alcohol. While all of these esters may possibly be used to advantage in the preparation of alkyd resins, most of the work reported here relates to the use of glycerol dilactate. This ester was reacted with various dibasic acids—namely, phthalic, maleic, azelaic, and sebacic—to produce divers resins. Attempts were then made to characterize these resins by elementary and practical tests and to compare them with the corresponding two-component alkyds, containing no lactic acid.

MATERIALS. In order to keep the research on a practical basis, commercial materials were used without further purification. Reagent-quality 85 per cent lactic acid and U. S. P. 95 per cent glycerol were employed. The water content of glycerol was verified by specific gravity determinations with the aid of tables given by Allen (1).

Resin-grade phthalic anhydride and maleic anhydride were used. The sebacic acid was supplied with the following specifications:

Acid number	Over 539 (theoretical, 555)
Water	Less than 1%
Ash	Less than 0.5%
Melting point	122–126° C.

The Martin Dennis Company kindly supplied us with quantities of exceptionally pure azelaic acid having an acid number of 592 (theoretical, 596).

GLYCEROL DILACTATE. All of the glycerol dilactate used in the subsequent syntheses of alkyd resins was prepared at one time. An 8-kg. batch was made by heating glycerol and lactic acid in a molal ratio of 1 to 2 at 190° C. in a conventional all-glass distilling apparatus, until no more water was evolved. It was thus possible to determine the quantity of water formed in the reaction, and this was found to correspond closely to the theoretical amount expected from the esterification. The removal of water was facilitated by bubbling a stream of carbon dioxide through the reaction mixture and also by operating at reduced pressure (4 to 5 cm. of mercury) near the end of the reaction. The product was a viscous, almost colorless and odorless liquid, readily soluble in water. Some of the properties were determined and are recorded in Table I.

All attempts to induce crystallization of the material proved unsuccessful. The amount of water evolved during the reaction corresponded to one mole for each mole of lactic acid. This shows that esterification has taken place, but it is not sufficient evidence to prove that the product is α,α'-glycerol dilactate (Figure 1, formula II). Other possibilities are: (A) a mixture of glycerol and polylactyllactic acids; (B) a mixture of mono-, di-, and trilactates of glycerol; and (C) glycerol monolactyllactate. The close agreement between the measured and theoretical molecular weights and the low value for free acids make possibility A appear unlikely. All attempts to distill the material resulted in decomposition yielding a crystalline solid and also liquids of variable compositions, possibly glycerol and lactyllactic acids. The material is soluble in chloroform but not in carbon tetrachloride. If it were merely a solution of type A or B, the different components would be expected to have different solubilities in a given chloroform-carbon tetrachloride mixture. When small amounts of carbon tetrachloride are added successively to a solution of "glycerol dilactate" in chloroform, successive fractions of the insoluble phase which is thus formed should

TABLE I. PROPERTIES OF GLYCEROL DILACTATE

	Experimental	Theoretical
Saponification equivalent	118.9	118.1
Free acid (mole H ion per gram equivalent)	0.04	0.0
Molecular weight, Rast method (6)	236.0	236.2
Density at 23° C.	1.268	....
Refractive index at 23° C. (Abbe)	1.4674	....
Molecular refraction	51.73[a]	51.65[b]

have varying saponification equivalents. However, no appreciable difference in the saponification equivalents was found. Furthermore, the solubility of the polylactyllactic acid in glycerol is very low. Possibilities A and B appear, therefore, to be ruled out, but the present data are insufficient to distinguish between α,α'-glycerol dilactate and glycerol monolactyllactate (Figure 1, formulas II and IV). Although further work on this point is contemplated, it would appear reasonable to assume that both α-hydroxyl groups of glycerol would enter into the reaction with equal avidity. It seems justifiable, therefore, to characterize this compound as α,α'-glycerol dilactate.

As previously stated, attempts to distill glycerol dilactate without decomposition have been unsuccessful. Conditions approximating molecular distillation were used in these experiments. The distillate, which is at first a water-clear sirup, obviously changes in composition as the distillation progresses, and finally, crystals begin to appear. These have been identified as dilactide:

$$CH_3—CH—C=O$$
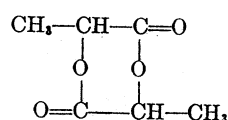
This is readily recrystallized from acetone-ether solution and has a melting point of 125.0° C.

Alkyd Resin Formation

EXPERIMENTAL PROCEDURE. The esterification of glycerol dilactate with the dicarboxylic acids was carried out in essentially the same manner as the primary esterification of glycerol with lactic acid. Because of the extent of the present exploratory investigations, measurements of water evolved, acidity, molecular weight, etc., were made on samples from a single reaction mixture, although it is recognized that greater accuracy on certain of these determinations would have been possible by running a number of specially adapted parallel experiments.

Two moles of glycerol dilactate were mixed at room temperature with three moles of the dicarboxylic acid in a one-liter, three-neck flask, having No. 24/40 ground-glass joints fitted, respectively, with a carbon dioxide inlet capillary, a thermometer which dipped into the reaction mixture, and a short-necked distilling head. This was connected in turn to a Liebig condenser, receiver, and trap cooled by solid carbon dioxide. The reaction flask was heated by means of an oil bath, and the temperature in the flask was held at 175° to 185° C. by manual control. During the course of the reaction the pressure in the system was gradually decreased so as to keep the charge boiling actively. At the same time care was taken to avoid the loss of any significant amounts of the reacting materials, such as volatile anhydrides. A stream of inert gas (carbon dioxide) was used to displace air and as means of agitation. The rate of admission of the gas was limited largely by the amount of foaming which could be tolerated in the flask.

At three intervals, the reaction flask was disconnected and weighed. Samples of the reaction mixture, each equivalent to 0.5 mole of glycerol and 0.75 mole of the dicarboxylic acid, were quickly removed for analysis and the flask was reconnected. At the same time the receiver and trap were set aside for measurement of the amount of distillate and were replaced by new ones. The remaining fourth of the batch was heated until signs of gelation began to appear, and this constituted the final sample. Heating periods represent the time elapsed after the reaction mixture reached 175° C. About 1.25 to 1.5 hours were required to bring the charge from room temperature to 185° C. The distillate, collected from receiver and solid carbon dioxide trap, was carefully redistilled, the solid residue was weighed and deducted from the total weight of the distillate, and the difference was reported as water. Acidities of the samples were determined by dissolving one-gram portions in neutral acetone and titrating them with 0.2 N alkali. The densities were determined by the pycnometer method and the viscosities by means of an Ubbelohde viscometer (21), both at 30° C. The average molecular weight

values were obtained from determinations of the freezing points of acetophenone solutions as recommended by Kienle and co-workers (12). For the solubility determinations, small amounts of the samples were placed in test tubes which contained the various solvents and were left overnight at room temperature. If the samples did not dissolve readily, they were heated on the steam bath.

RESULTS. The data for the reactions of glycerol dilactate with each of the four dicarboxylic acids are given in Table II. The pressures recorded in the third column are the approximate averages for the heating period between the taking of two samples.

The heating time to reach gelation (column 4) varies from 13 hours 30 minutes for the phthalate to 2 hours 40 minutes for the maleate. The corresponding two-component alkyd resins, without lactic acid, were also prepared at various temperatures, but no detailed study of their reaction course was made. The over-all reaction times for the lactic acid resins were found to be considerably longer, being approximately twice those for the glyceryl compounds of azelaic and sebacic acids, and roughly five times longer in the case of the compounds of phthalic and maleic acids. A similar retardation of the reaction rate is also observed when commercial modifying agents are used. Columns 5 and 6 give the values for the amounts of water and solid matter collected during the distillation. It should be emphasized that the amount of the reaction mixture decreased after the removal of each sample, and it was therefore necessary to multiply the experimental values for the water evolved by appropriate factors in order to obtain the amount of water which would have been obtained if the amount of the reaction mixture had remained unchanged.

The amounts of evolved water, as well as the acid numbers (seventh column) were used to calculate the degree of esterification at the various stages of the reaction, on the assumption that esterification is the only reaction which occurs. The method of calculation is the same as that used by Kienle and Hovey (11). The results are tabulated in the last column.

Kienle et al. (12, 13) made a careful study of the relation between the acid number and the amount of evolved water for glyceryl phthalate, maleate, and succinate. They showed that in the early part of the reaction there is an agreement between the amount of water collected and that calculated from the acid number, but that in the later stages deviations occur, which may be due to incomplete removal of water or to reactions other than esterification. In the present case the uncertainty in the values for evolved water does not permit such an analysis.

TABLE II. REACTION OF GLYCEROL DILACTATE WITH DICARBOXYLIC ACIDS

(Materials: 2 moles glycerol dilactate and 3 moles dicarboxylic acid)

Glyceryl Alkyd	Sample No.	Av. Pressure Cm. Hg	Heating Time Hours	Distillate Water Grams	Distillate Solid Grams	Acid No. Mg. KOH/g.	Degree of Esterification Calcd. from: Water evolved %	Degree of Esterification Calcd. from: Acid No. %
Lactylphthalate	1	70	5	18.5	0	150	67	60
	2	25	9.5	31.8	0	95	85	75
	3	25	12.5	40.3	0	87	90	78
	4	2.5	13.5	46.3	3.5	Gel	93	..
Lactylmaleate	1	50	0.7	2.9	1.1	230	53	48
	2	10	1.3	11.7	6.1	182	61	59
	3	7	2	16.3	10.3	146	65	67
	4	0.5	2.7	27.5	10.7	Gel	76	..
Lactylazelate	1	76	3	36.0	0	207	33	38
	2	7	3.5	55.3	0	173	51	49
	3	2	4	73.7	0.2	136	68	61
	4	1	4.3	85.3	1.3	107	79	70
Lactylsebacate	1	76	2	29.6	0	206	27	36
	2	20	2.8	53.4	0.1	157	50	52
	3	7	3.3	71.6	0.9	111	66	67
	4	2	3.8	85.6	1.0	95	79	72

The degree of esterification near the gelation point, as calculated from the acid values, is highest with the phthalate and lowest with the maleate. The values for azelate and sebacate are nearly the same. This would be expected from the similarity of the two molecules. The degrees of esterification of the glyceryl lactylphthalate and glyceryl lactylmaleate are nearly identical with the corresponding values previously obtained (12, 13) for glyceryl phthalate and glyceryl maleate. The comparison is shown in Table III.

TABLE III. DEGREE OF ESTERFICATION NEAR THE GELATION POINT

Glyceryl Alkyd	Degree of Esterification, %	Acid No.	Equivalent Weight	Ratios of: Equivalent weights	Acid No.
Phthalate	77	126	95.5	1.5	1.5
Lactylphthalate	78	86	144		
Maleate	68.5	231	71	1.7	1.6
Lactylmaleate	67	146	119		

While the incorporation of lactic acid in either the phthalate or the maleate does not produce a change in the degree of esterification, the acid numbers are much higher for the two-component resins than for those which include lactic acid. This apparent discrepancy is accounted for by the difference in equivalent weights. Thus, the ratio of equivalent weights of lactylphthalate to phthalate is equal to the reciprocal of the ratio of the corresponding acid numbers. The same is also nearly true for the maleates, as shown in the last two columns of Table III.

The average molecular weights were determined for the various samples of the reaction mixtures. The results are given in Table IV.

TABLE IV. AVERAGE MOLECULAR WEIGHTS

Sample No.	Glyceryl Lactyl-phthalate	Glyceryl Lactyl-maleate	Glyceryl Lactyl-azelate	Glyceryl Lactyl-sebacate
1	410	440	400	390
2	510	560	525	490
3	790	740	660	650
4	Gel	Gel	820	800

The highest values in each column represent conditions near the gelation point. These values range from 740 to 820 and show very small differences among the four dicarboxylic acids. The highest molecular weight value for glyceryl phthalate given by Kienle et al. (12) is 1120, that for glyceryl maleate (13) is 1050.

At the gelation point, therefore, the average molecular weight of the lactyl compounds is found to be lower than that of the corresponding two-component resins, in spite of the fact that the latter have the lower basic molecular weights. On the other hand, Table III shows that there is no difference in the corresponding degrees of esterification. Although these two facts at first appear to be contradictory, they may be regarded as supporting evidence of the view already presented in the introduction concerning the difference in the mechanisms of the esterification reactions of glycerol and glycerol dilactate, with the dicarboxylic acids.

Inasmuch as the glycerol molecule contains two primary, reactive hydroxyl groups, it may be assumed to behave at first as a dihydric alcohol and to form linear esterification products such as the "monomer" postulated by Kienle. Gelation does not occur until these monomers begin to inter-react and to form branched-chain molecules. In the case of glycerol dilactate there is no reason for assuming the formation of a similar linear monomer because all three available

hydroxyls are secondary alcohol groups, and they should react with approximately the same speed. Branched chains may therefore form during early stages of the reaction.

At the gelation point, which seems to be characterized by the same degree of esterification in the two- as in the three-component system, there are in the latter a larger number of molecules of lower molecular weight. Inasmuch as esterification may take place both within a molecule (intraesterification) and between two molecules (interesterification), the lower molecular weight may be accounted for by assuming that in the three-component systems there is a greater proportion of intraesterification than in the corresponding two-component systems. The intraesterified molecules, while smaller in size, may be capable of producing the gelation phenomenon by virtue of greater three-dimensional complexity.

The lower average molecular weight at the gelation point may also be due to the formation of smaller ester molecules by ester exchange in the three-component alkyds.

PROPERTIES IN SOLUTION. Portions of the samples of the reaction mixtures were dissolved in an equal weight of n-butyl acetate, and the 50 per cent solutions were used for the determination of density, viscosity, and compatibility with ester gum and nitrocellulose. For determination of the compatibilities, 50 per cent solutions of nitrocellulose and ester gum in butyl acetate were made up, and equal volumes of these and of the sample solutions were mixed in test tubes, warmed on the steam bath, and left overnight at room temperature. The results are shown in Table V.

With increasing degree of esterification there is a very slight increase in the density of the resin solutions.

The compatibility results merely determine whether one of the resins is thrown out of the solution by the presence of the other. With the exception of samples 2 and 3 of glyceryl lactylphthalate, all the materials were found to be compatible with nitrocellulose and ester gum.

The viscosity measurements corroborated the observation of earlier investigators that there is a rapid rise in the viscosity values just before gelation occurs.

EFFECT OF SOLVENTS. The effect of various solvents on the samples taken during the course of the reaction is given in Table VI. Two of the important properties of ideal alkyd resins are that they should be readily soluble in the commonly used paint solvents before gelation and be perfectly resistant to any solvent after baking. These properties are to some extent contradictory and can be approached only incompletely. In conventional alkyd resins the solubility in the precured stage is attained by the incorporation of modifying agents such as fatty acids or oils. It is evident from the results that the incorporation of lactic acid does not accom-

TABLE V. PROPERTIES OF THREE-COMPONENT ALKYDS IN 50 PER CENT BUTYL ACETATE SOLUTION

Glyceryl Alkyd	Sample No.	Density at 30° C., Grams/Cc.	Viscosity at 30° C., Centipoises	Compatibility with: Nitro-cellulose	Ester Gum
Lactylphthalate	1	1.060	29.2	Clear	Clear
	2	1.061	82.2	Turbid	Turbid
	3	1.062	500.0	Turbid	Turbid
	4	Insol.	...	....	....
Lactylmaleate	1	1.059	21.7	Clear	Clear
	2	1.060	32.9	Clear	Clear
	3	1.060	55.8	Clear	Clear
	4	Insol.	...	....	....
Lactylazelate	1	1.007	18.1	Clear	Clear
	2	1.008	23.0	Clear	Clear
	3	1.008	35.0	Clear	Clear
	4	1.012	120.0	Clear	Clear
Lactylsebacate	1	Sparingly sol.	...	....	....
	2	0.989	18.1	Clear	Clear
	3	0.991	41.1	Clear	Clear
	4	0.992	104.0	Clear	Clear

TABLE VI. EFFECT OF SOLVENTS

Glyceryl Alkyd	Sample No.	Water	Ethyl Alcohol	Acetone	Butyl Acetate	Toluene	Petroleum Ether
Lactylphthalate	1	Becomes opaque	Sol.	Sol.	Sol.	Swells	Insol.
	2	Becomes opaque	Partly sol.	Sol.	Sol.	Swells	Insol.
	3	Becomes opaque	Swells	Sol.	Sol.	Slight swelling	Insol.
	4	Becomes opaque	Swells	Swells	Swells	Insol.	Insol.
Lactylmaleate	1	Sol.	Sol.	Sol.	Sol.	Swells	Insol.
	2	Partly sol.	Sol.	Sol.	Sol.	Swells	Insol.
	3	Slight effect	Partly sol.	Sol.	Sol.	Insol.	Insol.
	4	Slight effect	Slight effect	Swells	Swells	Insol.	Insol.
Lactylazelate	1	Partly sol.	Sol.	Sol.	Sol.	Partly sol.	Insol.
	2	Slight effect	Sol	Sol.	Sol.	Partly sol.	Insol.
	3	Slight effect	Sol.	Sol.	Sol.	Partly sol.	Insol.
	4	Slight effect	Partly sol.	Sol.	Sol.	Partly sol.	Insol.
Lactylsebacate	1	Partly sol.	Sol.	Sol.	Partly sol.	Partly sol.	Insol.
	2	Partly sol.	Sol.	Sol.	Sol.	Partly sol.	Insol.
	3	Some swelling	Sol.	Sol.	Sol.	Swells	Insol.
	4	Some swelling	Partly sol.	Sol.	Sol.	Swells	Insol.

plish the same solubilizing effect as do the known modifying agents. Acetone is a good solvent and butyl acetate a fair solvent for these lactic acid alkyds.

Comparative Properties of Alkyd Resins

When the conventional two-component as well as the new three-component alkyd resins are heated beyond the gelation stage, they become insoluble and infusible. Phthalates and maleates become hard, while the corresponding azelates and sebacates exhibit flexible, rubberlike properties. An attempt has been made to characterize these solid resins by various tests and to determine any novel properties which may be attributed to the presence of lactic acid.

TABLE VII. ABSORPTION TESTS ON DISKS

Glyceryl Alkyd	Initial Weight	Gain in Weight 24 hours		Gain in Weight 72 hours	Weight Loss after Reconditioning	Amount Leached in 72 Hr.	Total Amounts Absorbed in 72 Hr.	
	Gram	Gram	%	Gram	Gram	%	Gram	%
				Water Absorption				
Phthalate	17.508	0.022	0.13	0.040	0.023	0.13	0.063	0.36
Lactylphthalate	17.108	0.065	0.38	0.103	0.062	0.36	0.165	0.97
Maleate	18.005	0.077	0.43	0.123	0.005	0.03	0.128	0.71
Lactylmaleate	18.218	0.070	0.38	0.122	0.014	0.08	0.136	0.75
Azelate	19.465	0.136	0.67	0.246	0.052	0.27	0.298	1.53
Lactylazelate	15.597	0.134	0.86	0.202	0.085	0.53	0.287	1.84
Sebacate	15.110	0.131	0.87	0.197	0.068	0.45	0.265	1.76
Lactylsebacate	15.425	0.135	0.88	0.207	0.111	0.72	0.318	2.06
				Gasoline Absorption				
Phthalate	17.1765	0.0018	0.01	0.0035	0.072	0.42	0.076	0.44
Lactylphthalate	17.6119	0.0031	0.02	0.0061	0.122	0.69	0.128	0.73
Maleate	19.0282	0.0026	0.02	0.0058	0.026	0.13	0.031	0.16
Lactylmaleate	18.2050	0.0040	0.02	0.0060	0.029	0.16	0.035	0.19
Azelate	20.3445	0.092	0.45	0.1695	0.044	0.22	0.213	1.05
Lactylazelate	15.9881	0.076	0.47	0.1199	0.006	0.04	0.126	0.79
Sebacate	15.9344	0.181	1.76	0.3156	−0.003	0.00	0.313	1.97
Lactylsebacate	15.5267	0.079	0.51	0.1313	0.003	0.02	0.134	0.86

Direct comparison of the new alkyd resins with commercial products would be desirable, but inasmuch as the conventional alkyd resins are usually modified before coming on the market, the two-component materials had to be specially prepared for these tests.

In the present study testing was limited to certain basic properties of paint resins—namely, water and gasoline absorption, shock resistance (dropping ball) for the hard and rigid resins and hardness for the flexible resins. The tests were conducted on disks of the cured resins. Films of the resin on metal were also prepared and were tested for flexibility and for water resistance.

DISKS. Disks, 2, 3, and 4 inches (5.1, 7.6, and 10.2 cm.) in diameter and $1/_8$ inch (3.18 mm.) thick, were cast in aluminum foil dishes from the various resins prior to gelation and cured in an air oven at 130° to 155° C. for 2 to 4 days. After heating for 1 to 2 days, depending on the particular batch, the dishes were stripped off and the disks were turned over to facilitate the cure.

Water and gasoline absorption tests were made on the 3-inch disks by soaking them in these liquids under identical conditions at room temperature, 17° to 25° C. The absorption values were determined for 24- and 72-hour periods. At the end of the 72-hour period the samples were dried and reconditioned by baking for 16 hours and were then reweighed. The weight loss attributable to leaching was added to the gain by absorption and has been recorded as total absorption. The results are given in Table VII.

The results indicate that the lactyl compounds absorb somewhat more water than the corresponding two-component alkyds. The same is true for the gasoline absorption of phthalate and maleate. The gasoline absorption of lactylazelate and sebacate is less than that of the corresponding two-component resins.

Shock resistance was measured by dropping steel balls weighing 16 and 225 grams, respectively, from increasing heights onto 3-inch disks which rested on a rubber ring. Ten or more disks of each composition were tested. The procedure was to start with a light ball at low elevation and to increase the elevation for each successive impact until the sample broke. A great deal of variation was found to exist among the disks of the same material, and only the extreme limits for each material are, therefore, reported in Table VIII.

The data indicate that glyceryl phthalate is stronger than glyceryl lactylphthalate, while glyceryl lactylmaleate appears

TABLE VIII. FALLING BALL TESTS

Glyceryl Alkyd	Weight of Ball, Grams	Height in Feet (Meters) Average	Minimum	Maximum
Phthalate	16	12.2 (3.7)	2 (0.6)	......
	225	0.9 (0.3)	.....	5.5 (1.7)
Lactylphthalate	16	2.5 (0.8)	2 (0.6)	4 (1.2)
Maleate	225	3.2 (1.0)	2 (0.6)	7 (2.1)
Lactylmaleate	225	4.9 (1.5)	3 (0.9)	8 (2.4)
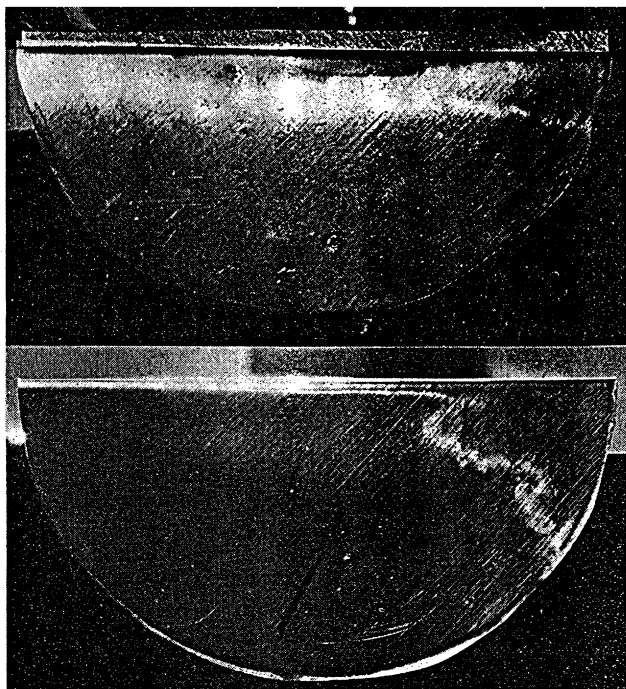
FIGURE 3. FLEXIBILITY OF FILMS OF GLYCERYL MALEATE (*above*) AND OF GLYCERYL LACTYLMALEATE ON ALUMINUM FOIL

FILMS. Films 0.001 to 0.004 inch (0.025 to 0.10 mm.) thick were prepared by evaporating butyl acetate solutions of the uncured resins on aluminum foil and baking at 140° C. for 16 to 24 hours. They were tested for flexibility and for resistance to water and gave results as shown in Table X.

To determine the water resistance, the foils bearing the films were immersed in water at room temperature for a total of 150 hours. Observations were made at various intervals after the first hour. Both of the phthalate samples became badly chalked after 1 hour. The other samples appeared unaffected in this respect. At the end of 150 hours glyceryl sebacate and glyceryl lactylsebacate showed very slight chalking, while both azelates and both maleates appeared to be unaffected.

TABLE IX. HARDNESS TESTS

(Pusey and Jones plastometer, 1-kg. load, ¹/ᵣ-inch ball tip)

Glyceryl Alkyd	Thickness of Disk, Mm.	Indentation, 0.01 Mm.
Sebacate	3.84	71
	6.94	95
	11.36	125
	13.61	126
Lactylsebacate	3.35	84
	6.16	103
	9.57	127
	12.47	139
Azelate	2.22	50
	4.17	117
	7.14	172
	10.65	195
Lactylazelate	3.60	75
	6.01	104
	9.50	120
	13.09	161

to be stronger than glyceryl maleate. These results, however, cannot be regarded as being conclusive, because slight differences in the conditions under which the samples were prepared markedly affected the strength of the resin disk.

Variations in individual samples were also found to exist in the mechanical testing of the azelate and sebacate disks by the Pusey and Jones plastometer (*17*).

The hardness values listed in Table IX fall well within the limits for those of various kinds of rubber. The specimen thickness required to obtain a limit value is much in excess of the usual 15 × indentation; in fact, no limit value is reached with specimens even as thick as 0.5 inch (1.27 cm.). The disks show a peculiarity in that the recovery of these materials upon removal of the load is instantaneous and complete.

In view of the fact that all of the materials tested show relatively low mechanical strength, as well as large variations between individual disks, it may be assumed that conditions on the inside of heavy layers of these materials are not conducive to a complete and uniform cure.

At the end of the 150-hour soaking period it was also found that maleate, phthalate, and the lactylsebacate films adhered firmly to the metal. The others were loose and pulled off easily. The adherence of the film to the metal was visibly improved by the presence of lactic acid in the case of the sebacate. This result is unlike the water absorption result on disks. No apparent differences were observed in the other cases.

A striking and demonstrable effect, directly traceable to the lactic acid, was found on folding and straightening out again 0.005-inch (0.127-mm.) aluminum foil sheets which had previously been coated with various thicknesses of glyceryl maleate and glyceryl lactylmaleate and baked for 16 hours at 140° C. While the glyceryl maleate coatings cracked invariably on the first bending and became separated from the metal, the glyceryl lactylmaleate appeared to withstand as much flexing as the underlying aluminum, and showed no appreciable damage even in thicknesses of 0.004 inch. Figure

TABLE X. TESTS ON FILMS*

Glyceryl Alkyd	Thickness of Film, Mm.	Effect of Folding	Effect of Water after: 1 hr.	96 hr.	150 hr.	Adherence to Metal after 150-Hr. Soaking
Phthalate	0.08	Break	Chalky	Chalky	Chalky	Good
Lactylphthalate	0.05	Break	Chalky	Chalky	Chalky	Good
Maleate	0.07	Break	Clear	Clear	Clear	Good
Lactylmaleate	0.08	No break	Clear	Clear	Clear	Good
Azelate	0.07	No break	Clear	Clear	Clear	Bad
Lactylazelate	0.07	No break	Clear	Clear	Clear	Bad
Sebacate	0.06	No break	Clear	Clear	Slightly chalky	Bad
Lactylsebacate	0.11	No break	Clear	Clear	Slightly chalky	Good

* These films were prepared by evaporating butyl acetate solutions of the resins on aluminum foil 0.07 mm. thick. The films were baked at 140° C. for 24 hours. The folding test was performed soon after baking and was followed by the water immersion test.

3 shows the effect of folding in two of circular 0.005-inch (0.13-mm.) aluminum foil disks which have been coated with 0.003-inch (0.076-mm.) films. The broken film of glycerol maleate can be seen protruding along the folded top edge of the disk. The glycerol lactylmaleate film shows no rupture on bending. In this instance the lactic acid produces an effect which is ordinarily achieved by the so-called modifying agents.

ELECTRICAL PROPERTIES. The dielectric constant and the power factor at 1 and 100 kilocycles, and the volume resistivity of these resins were determined by A. H. Scott of the National Bureau of Standards. These measurements were made on $1/8 \times 4$ inch (0.318 × 10.2 cm.) disks prepared in the same manner as outlined previously. In general, the properties desired in dielectric materials are high volume resistivity, low dielectric constant, and low power factor. For many applications, however, the choice of a dielectric depends as much on its physical and mechanical properties as on its electrical properties. Averages of the results obtained on two or three disks of each material are listed in Table XI, together with those on three commercial materials.

TABLE XI. ELECTRICAL PROPERTIES

Glyceryl Alkyd	Vol. Resistivity, Ohm-Cm.	Dielectric Constant		Power Factor	
		1 kc.	100 kc.	1 kc.	100 kc.
Phthalate	10×10^{15} (4)	5.0 (14)	...	0.01 (14)	....
	15×10^{15}	4.1	4.0	0.0073	0.0200
Lactylphthalate	8×10^{15}	3.8	3.7	0.0053	0.0144
Maleate	9×10^{15}	4.2	4.0	0.0112	0.032
Lactylmaleate	9×10^{15}	3.9	3.8	0.0067	0.0212
Azelate	6×10^{11}	6.4	5.9	0.0095	0.061
Lactylazelate	5×10^{11}	6.9	5.3	0.0227	0.131
Sebacate	2×10^{11}	6.4	6.1	0.0077	0.045
Lactylsebacate	6×10^{11}	6.7	5.5	0.0208	0.121
Methacrylate	5×10^{16}	3.3	3.0	0.045	0.029
Polystyrene	10^{17}	2.6	2.6	0.0001	0.0001
Ethylcellulose	10^{14}	2.9	2.7	0.010	0.005

Varnish Preparations from Alkyds

The three-component alkyds were used in the preparation of varnish cooks with drying oils and phenoplastic resins in accordance with available formulas. These preparations were found to be soluble in the usual inexpensive paint thinners. Although extensive tests have not yet been made, no pronounced differences have been found between varnishes containing these resins and conventional preparations. Investigations are now under way to develop advantageous formulas and to determine the comparative weathering resistance of the new coating composition.

Economic Considerations in Making Alkyd Resins

Lactic acid is produced commercially by the bacterial fermentation of various sugars. Glucose from cornstarch, lactose from milk whey, and sugar cane molasses are all used, and the supply of these agricultural materials is practically unlimited. Furthermore, it is reasonable to assume that the competitive producers of lactic acid can introduce these sugars into the fermentation process at about 1 to 4 cents per pound.

The employment of lactic acid in the preparation of alkyd resins depends on the presence of two essential chemically reactive groups—namely, hydroxyl and carboxyl. Unlike other similar hydroxycarboxylic acids, such as gluconic, citric, and tartaric, lactic acid is thermally stable. It can be heated to 210–240° C. to produce a light-colored polymer of relatively low acid number (10), while the hydroxy acids of higher molecular weight decompose with the loss of water and carbon dioxide to yield dark reaction products.

Lactic acid used as a component of alkyd resins may lead to an inferior product, a resin with no marked changes in chemi-

cal or physical properties, or a product which is superior to the comparable two-component condensation products. Our limited investigations do not indicate the formation of products which are inferior with respect to flexibility, electrical properties, or attack by water or solvents. As a matter of fact, the modification of glycerol maleate resins with lactic acid leads to improved products at a lower raw material cost.
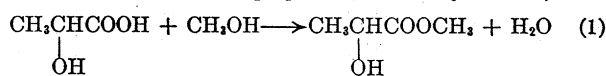
Assuming that the lactic acid merely modifies the alkyd resin and imparts neither deleterious nor advantageous properties, it would enjoy a large market only if it became available at a cost which was lower than the present price levels of glycerol (12 cents), phthalic anhydride (14 cents), and maleic anhydride (30 cents). Current market prices indicate that lactic acid can now be obtained at about 10 to 30 cents per pound (100 per cent basis), depending on specifications. A reduction in the current price of a suitable grade of lactic acid would stimulate the interest in, and use of, this product. It is not unreasonable to expect a progressive lowering of the price, as well as an increase in the purity of this acid, with increased production and improved operating technics.

In 1937 the domestic production of alkyd resins was over 61 million pounds, and it rose to 76 million pounds in 1939. If the cost of lactic acid can serve as an economic ceiling for the ingredients entering into the preparation of such resins, it may become one of the industrially important organic chemicals of the future.
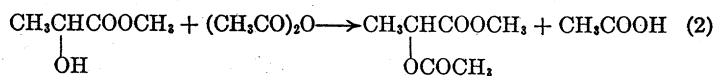
Methyl Acrylate Synthesis from Lactic Acid

Lactic acid can also be used for the preparation of acrylic acid esters. Ritchie, Jones, and Burns (19) and Smith and Claborn (20) reported on the preparation of unsaturated nitriles and esters by the pyrolysis of corresponding acylated α-hydroxy acids. Their preparation of methyl acrylate from lactic acid may be represented by the following three reactions:
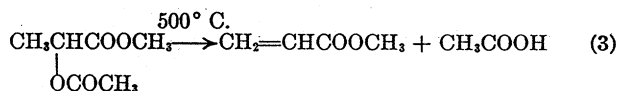
Primary esterification: preparation of methyl lactate,

$$\underset{\overset{|}{OH}}{CH_3CHCOOH} + CH_3OH \longrightarrow \underset{\overset{|}{OH}}{CH_3CHCOOCH_3} + H_2O \quad (1)$$

Secondary esterification: preparation of methyl α-acetoxypropionate,

$$\underset{\overset{|}{OH}}{CH_3CHCOOCH_3} + (CH_3CO)_2O \longrightarrow \underset{\overset{|}{OCOCH_3}}{CH_3CHCOOCH_3} + CH_3COOH \quad (2)$$

Pyrolysis: preparation of methyl acrylate

$$\underset{\overset{|}{OCOCH_3}}{CH_3CHCOOCH_3} \overset{500°\ C.}{\longrightarrow} CH_2{=}CHCOOCH_3 + CH_3COOH \quad (3)$$

This synthesis was given detailed consideration with the hope of devising practical ways of obviating the acetylation or pyrolytic steps and thus providing a more economical procedure. In this effort we have not yet been successful. Our economic appraisal of the process for the preparation of methyl acrylate from lactic acid as compared with the competitive synthesis from ethylene and ethylene oxide is given in Tables XII to XIV. In computing the material costs, the best reported yields in the synthesis from lactic acid have been used. For the competitive processes the yields and material costs are based on information derived from industrial and literature sources.

From an examination of the preceding cost data, as well as from a consideration of other factors involved in the use of either lactic acid, ethylene, or ethylene oxide, respectively, as raw materials in the synthesis of methyl acrylate, it appears that the process based on lactic acid is burdened with the

TABLE XII. METHYL ACRYLATE SYNTHESIS FROM LACTIC ACID

Conversion of lactic acid to methyl lactate

90 lb. (lb. mole) lactic acid at 10¢	$ 9.00
32 lb. (lb. mole) methanol at 6¢	1.92[a]
4 lb. sulfuric acid	0.02
Cost of raw materials	$10.94
Yield, 90% of theory (104 × 90)	94 lb.
Cost of chemicals per lb. methyl lactate	
With lactic acid at 10¢	$ 0.116
With lactic acid at 8¢	0.097
With lactic acid at 5¢	0.069
Present price of methyl lactate	0.20

Preparation of methyl α-acetoxypropionate

104 lb. (lb. mole) methyl lactate at 11.6¢	$12.06
102 lb. (lb. mole) acetic anhydride at 10¢	10.20
Cost of raw materials	22.26
Credit 60 lb. acetic acid at 5¢	3.00
Net cost of raw materials	$19.26
Yield, 95% theory (146 × 95)	139 lb.
Cost of chemicals per lb. methyl α-acetoxypropionate	$ 0.139

Pyrolysis of methyl α-acetoxypropionate

146 lb. (lb. mole) methyl α-acetoxypropionate at 13.9¢	$20.29
Credit for 40 lb. acetic acid at 5¢	2.00
Net cost of chemicals	$18.29
Yield methyl acrylate, 88% theory (86 × 88)	75.7 lb.
Cost of chemicals per lb. methyl acrylate	
With lactic acid at 10¢	$ 0.24
With lactic acid at 8¢	0.21
With lactic acid at 5¢	0.17

[a] Assuming 100% recovery of excess methanol.

TABLE XIII. METHYL ACRYLATE SYNTHESIS VIA ETHYLENE CHLOROHYDRIN

Preparation of ethylene chlorohydrin

28 lb. ethylene at 3¢	$ 0.84
71 lb. chlorine at 2¢	1.42
30 lb. lime at 0.5¢	0.15
Cost of raw materials	$ 2.41
Yield, 90% theory (80.5 × 90)	72.5 lb.
Cost of chemicals per lb. chlorohydrin	$ 0.033

Preparation of ethylene cyanhydrin

80.5 lb. ethylene chlorohydrin at 3.3¢	$ 2.68
50 lb. sodium cyanide at 10¢	5.00
Cost of raw materials	$ 7.68
Yield, 95% theory (71 × 95)	67.5 lb.
Cost of chemicals per lb. cyanhydrin	$ 0.114

Hydrolysis of cyanhydrin to methyl acrylate

71 lb. cyanhydrin at 11.4¢	$ 8.08
32 lb. methanol at 6¢	1.92
98 lb. sulfuric acid at 1¢	0.98
Cost of raw materials	$10.98
Yield, 75% theory (86 × 75)	64.5 lb.
Cost of chemicals per lb. methyl acrylate	
With ethylene at 3¢	$ 0.170
With ethylene at 5¢[a]	0.180

[a] Advices from reliable sources indicate that ethylene is valued at not over 2¢ per pound in cracking plants.

TABLE XIV. METHYL ACRYLATE SYNTHESIS VIA ETHYLENE OXIDE

Preparation of ethylene oxide

28 lb. ethylene at 3¢	$ 0.84
Air, AgO catalyst	0.16
Cost of raw materials	$ 1.00
Yield, 50% theory (44 × 50)[a]	22 lb.
Cost of chemicals per lb. ethylene oxide	$ 0.0455

Preparation of ethylene cyanhydrin

44 lb. ethylene oxide at 4.55¢	$ 2.00
50 lb. sodium cyanide at 10¢	5.00
98 lb. sulfuric acid at 1¢	0.98
Cost of raw materials	$ 7.98
Yield, 95% theory (71 × 95)	67.5 lb.
Cost of chemicals per lb. cyanhydrin	$ 0.118

Conversion of ethylene cyanhydrin to methyl acrylate

71 lb. ethylene cyanhydrin at 11.8¢	$ 8.40
32 lb. methanol at 6¢	1.92
98 lb. sulfuric acid at 1¢	0.98
Cost of raw materials	$11.30
Yield, 75% theory (86 × 75)	64.5 lb.
Cost of chemicals per lb. methyl acrylate	$ 0.175

[a] Yields of 93% have been reported (16).

following disadvantages: (a) The cost of essential chemicals is greater; (b) pyrolysis, as the final step in the synthesis, results in a product of lower purity; (c) the procedure is practical only for the preparation of the methyl ester, whereas the competitive methods are useful for other acrylates as well; (d) the process, to be practical, depends on the efficient recovery and purification of acetic acid, and its disposal at a favorable price.

Conclusions

1. A new type of alkyd resin has been prepared, starting from glycerol dilactate as the polyhydric alcohol, and phthalic, maleic, azelaic, or sebacic acid as the dicarboxylic acid.

2. Some of these resins have, without further addition, a degree of flexibility which is imparted to the commercial alkyd resins only by modifying agents. This is readily demonstrable with the maleate.

3. The physical properties of these alkyd resins are similar to those of the known commercial alkyd resins; therefore the possibility of using lactic acid in the manufacture of coating compositions appears to be largely dependent upon its price.

4. Modification of these alkyd resins with drying oils brings about solubility in low-cost paint thinners.

5. These new three-component resins gel at a lower average molecular weight than the corresponding two-component alkyds. This phenomenon is attributed to a different reaction mechanism, owing to the presence of three secondary alcohol groups in glycerol dilactate.

6. Although fairly good yields from the conversion of lactic acid into methyl acrylate are obtained, it is doubtful whether this procedure can compete with the syntheses from ethylene or ethylene oxide.